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I, JANENE PEISKER, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2004901900 for a patent by AUSMELT LIMITED as filed on 07 April 2004.



WITNESS my hand this
Eighteenth day of April 2005

A handwritten signature in cursive script, appearing to read 'J. Peisker'.

JANENE PEISKER
TEAM LEADER EXAMINATION
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AUSTRALIA
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PROVISIONAL SPECIFICATION

APPLICANT: **AUSMELT LIMITED**
Invention Title: **PROCESS FOR COPPER CONVERTING**

The invention is described in the following statement:

PROCESS FOR COPPER CONVERTING

Field of the Invention

This invention relates to a process for the production of blister copper.

5 • Background to the Invention

The production of blister copper to date has been dominated by use of Pierce-Smith converters. However these converters are progressively falling further behind environmentally acceptable standards for off-gas emissions. In more recent times, technologies such as those developed by Outokumpu and
10 Mitsubishi have been adapted to the production of blister copper. These not only provide an improvement in environmental performance over the Pierce-Smith converters, but also improve the scale of operation and productivity. Still more recent is the proposal of Edwards et al disclosed in US patent 5888270, issued 30 March 1999.

15 The proposal of Edwards et al utilises what is referred to as a lance based process. More specifically, the process uses a top-submerged injection lancing furnace in which an injection lance is lowered from above a molten bath to submerge a discharge tip at its lower end for injection within the bath. The bath consists of a continuous slag phase, in particular of a calcium ferrite slag, which
20 floats on a continuous molten blister copper phase. Matte and/or concentrate, together with a suitable flux, is added to the slag phase while that phase is agitated by the submerged injection of an oxidizing gas capable of reacting with the matte and/or concentrate to form blister copper. The lance tip is located deep within the slag phase to ensure that a substantial proportion of injected oxidizing
25 gas contacts the blister copper phase.

It is suggested in Edwards et al that contact of oxidizing gas with the blister copper oxidises the blister copper and generates copper oxide which floats to an interface between the slag and blister copper phases. It is suggested that the copper oxide reacts with matte or concentrate which reaches the interface, or alternatively is dissolved or dispersed in the slag to react with the matte or concentrate. It also is contended that the copper oxide assists desulphurisation of the copper and improves the utilization of oxygen by the sulphur with concomitant reduction of the sulphur content of the blister copper and of copper losses to the slag. However, low sulphur blister copper contents are said to be achieved by injecting oxygen directly into the copper layer, as distinct from merely deeply injecting the oxygen in the slag for contacting the copper layer at its interface with the slag layer.

The present invention also relates to a process for producing blister copper by top-submerged injection. However, the process of the invention is directed to a process which obviates the need for a substantial proportion of an oxidizing gas to make contact with the blister copper phase, or for any need for injection into the copper phase through its interface with the continuous slag phase.

Broad Outline of the Invention

The present invention provides a process for converting a copper sulphide matte to blister copper, wherein the process includes the steps of:

adding the copper sulphide matte and flux, to a suitable, agitated slag phase; and

injecting, from a discharge tip at the lower end of a top-submerged lance, an oxidizing gas suitable for reacting with the matte to produce blister copper which forms or adds to a continuous blister copper phase below the slag phase;

wherein the lance tip is located within the slag phase at a depth enabling the injected gas to agitate the slag phase, and to react with copper sulphide matte dispersed therein, while precluding a substantial proportion of the gas from contacting the continuous blister copper phase.

5 The process of the invention is conducted with a substantial depth of slag. This is a depth which enables agitation of the slag phase by the top-submerged injection therein without a stream or jet of the injected gas passing through to the lower surface of the slag phase. The actual depth of slag can vary with a number of factors, including the size and shape of the furnace or reactor, and the number
10 of and spacing between lances where more than one is used. The depth of slag may range from a minimum of about 500mm up to about 2m, preferably about 700mm to about 1.7m.

The depth of the slag phase and the requirements for top-submerged injection in the present invention have a number of practical benefits. A first
15 benefit is that start-up of the process is facilitated in that a blister copper phase need not initially be present at all or to a significant extent. In contrast, the process of Edwards et al necessitates the presence of a blister copper phase at the outset, in order to prevent gas which is to contact that phase from impinging on refractory lining of the furnace, or to use a modified mode of operation until a
20 sufficient depth of blister copper has been produced.

A further benefit of the requirements of the present invention for top-submerged injection is that injection is able to be at a significant height above the lower surface of the slag phase and need not be directed towards that surface. Thus, the injection is able to be at a mid-region of the slag phase, or nearer to the
25 top of the slag phase where this is relatively shallow, and directed outwardly from the lance tip. Thus, the injected gas is able to be directed downwardly and

outwardly in a plurality of streams angularly spaced around the tip of the lance. In this way, the gas more readily is able to agitate the entire slag phase body, thereby facilitating uniform dispersal of the copper sulphide matte throughout the slag phase. This enables substantially maximum utilization of the slag phase as a reaction medium in which the matte is able to be oxidised, thereby enhancing the overall efficiency of operation of the process. The process of the present invention therefore may be conducted with a lance which has an outlet tip provided with a plurality of suitable oriented outlets for providing a plurality of downwardly and outwardly directed streams. However, the lance more preferably has vanes or swirlers which impart helical flow to gas passing therethrough for injection, to maximise mixing of the gas with, and turbulence in, the slag phase. In each case the lance is of a form that provides injected gas with a radial injection component to promote dispersion of the gas into the slag phase and avoid penetration of gases into the metal phase.

Since the slag is the reaction medium for conversion of the copper sulphide matte to blister copper, the volume of the slag phase is a factor which contributes to the rate of production of blister copper. The indicated requirements for top-submerged injection enable use of a relatively large slag phase volume for a given reactor and, hence, a relatively high rate of production of blister copper. In contrast, the mode of injection required by the process of Edwards et al tends to confine the effective volume of slag phase to a lower region of the available slag phase volume. Certainly, in the process of Edwards et al, there can be a substantial depth of slag phase. However, the upper region of the slag phase tends to provide a less effective part of the overall volume for efficient production of blister copper and the extent of the upper region increases with increasing slag phase depth. Also, with increasing depth of the slag phase, there is an increased

risk of problems arising from vibration of the furnace induced by the high velocity and mass flow rate of the injected gas.

A still further benefit of the requirements of the present invention for top-submerged injection is the reduction of competing reactions. Thus, contrary to the proposal of Edwards et al, it is preferable to avoid oxidation of copper in the blister copper phase and the present invention facilitates this avoidance.

Overall, there are significant differences between the present invention and the process of Edwards et al in relation to the slag phase. Edwards et al teaches the use of a deep slag layer in order to:

- 10 (a) allow time for the copper sulphide matte or copper concentrate to melt and react with the slag;
- (b) maintain the matte as a dispersion - but reaction between the matte and slag is maximised while reaction between the matte and blister copper is to be minimised; and
- 15 (c) ensure the slag is well agitated by the injected gas while injecting a substantial portion of the injected oxygen into the blister copper by a deeply submerged lance, in the maintained deep slag phase.

The injection of a substantial portion of the oxygen into the blister copper will result in a lower region of the slag phase in which blister copper is dispersed. However, reaction between matte (in the slag) and blister copper (dispersed in a lower region of the slag) is to be minimised. Thus, it is evident that substantially all or a substantial proportion of the matte needs to be reacted to produce blister copper before it reaches the lower region of the slag phase. However, it is difficult enough to minimise reaction between matte and blister copper in the process of
25 converting matte to blister copper without, at the same time, dispersing blister

copper from the layer of blister copper phase into the region of the slag in which the matte is dispersed.

In contrast, the present invention, while able to accommodate a similar depth of slag phase, does not necessitate this. Also, regardless of the slag phase
5 depth, the present invention enables and benefits from a slag phase in which matte is relatively uniformly or homogeneously dispersed, rather than one in which compositional strata or gradients are to be generated. Also, the invention obviates the need for injection into the blister copper phase, and that phase is able to be maintained as a relatively quiescent phase in which blister copper
10 being produced by the process is able to collect. Thus, with continuous converting of matte, the process of the invention is considerably more amenable to tapping of blister copper, either continuously or at intervals, without the need to interrupt top submerged injection.

As indicated above, the proposal of Edwards et al is illustrated by reference
15 to a calcium ferrite slag. That slag preferably is highly oxidised and has copper oxide, calcium oxide, ferric and ferrous oxides, and silica as its main components. The use of a calcium ferrite slag is in accord with recent recommended and accepted practice, such as illustrated by the use of calcium ferrite slags in the conversion stage of the Mitsubishi process. However, there are significant
20 difficulties with the use of calcium ferrite slags in copper converting. As a result, there recently has been work on investigating the use of ferrous calcium silicate slags.

Calcium ferrite slags are used in the converting stage of the Mitsubishi process. This is in contrast to the iron silicate slags used in the first, smelting
25 stage of the Mitsubishi process, and also used throughout Pierce-Smith converting. The calcium ferrite slags present a wide, homogeneous liquid area

when mixed with iron oxides. This enables them to absorb iron oxide generated during converting. The calcium ferrite slags thus are able to avoid troublesome magnetite precipitation and so obviate the risk of slag foaming which magnetite precipitation can cause with iron silicate slags. However, the calcium ferrite slags have their own problems. One major problem with calcium ferrite slags results from their high fluidity/low viscosity. Also, they cause excessive refractory damage, and have a low lead removal ratio. Additionally, the calcium silicate slags retain substantial quantities of copper oxide, while they are not suitable for subsequent treatment by flotation or reduction in conventional slag cleaning furnaces for the recovery of copper. This limits the treatment of the resulting slag to recycling as a solid to a smelting stage. Moreover, calcium ferrite slags have little tolerance for silica which may enter the process as impurities in the feed streams either because silica is inherent in the feed materials or inadvertently through contamination. The extent of the problems with calcium ferrite slags is reflected by the move to ferrous calcium silicate slags, despite these being relatively untested on a commercial scale.

In an important form of the present invention, the slag phase is an iron based silicate (fayalite or olivine) slag, although other slags can be used. In other contexts, the iron based silicate slag system has known problems. We have found that these problems can be overcome or avoided with use of the present invention. Also, we have found that the known benefits of the iron based silicate slags are able to be retained with use of the present invention. Thus, the process of the invention is able to be based on a slag phase with which the industry is familiar. Also, in converting copper sulphide matte, it is possible to integrate the process with an existing smelting plant producing the matte, with the slag resulting from the process of the invention able to be treated readily by way of recycle,

flotation or reduction to recover contained copper. Moreover, blister copper product is able to be of a required commercial quality, such as with respect to a low sulphur content.

The preferred iron based silicate slag used for the slag phase in the present invention has a composition which is significantly different to the calcium ferrite slag taught by Edwards et al. This is illustrated by reference to particularly preferred compositional ranges for the iron based slag shown in the following Table 1.

Table 1 : Slag Comparison

	<u>Fe/SiO₂</u>	<u>CaO/Fe</u>	<u>CaO/SiO₂</u>
Edwards et al	7.14 - 66.67*	0.15 - 0.7	5 - 10
Invention	1.14 - 1.55	0.15 - 0.92	0.22 - 1.11

* calculated based on cited CaO/Fe and CaO/SiO₂ ratios

The differences between the composition of calcium ferrite slags and the iron based silicate slags of the present invention are further illustrated by the accompanying drawings. In the drawings, Figure 1 shows the phase equilibrium diagram for the CaO - "Fe₂O₃" - SiO₂ oxide system (as published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960), and Figure 2 is a simplified enlargement of the lower right hand corner of the diagram of Figure 1. It is to be understood that this is a two dimensional ternary projection of a quaternary system that includes Fe²⁺, due to the varying levels of both Fe³⁺ and Fe²⁺ in the respective slag systems.

In Figures 1 and 2, there are three regions of the diagram which have been highlighted. The first region A is the area containing the calcium ferrite slags of Edwards et al. The region B contains the iron based silicate slags preferred for

the present invention, while region C within region B contains the particularly preferred iron based silicate slags for use in the present invention.

Figure 3 is an alternative illustration of the quaternary system shown in Figures 1 and 2. In Figure 3, an attempt is made to represent the regions A, B and C with allowance for both Fe_2O_3 and FeO .

The region A, as shown in Figures 1 to 3, is constrained by the lines $\text{CaO}/\text{SiO}_2 = 5$ and $\text{CaO}/\text{SiO}_2 = 10$ and by the lines $\text{CaO}/\text{Fe} = 0.15$ and $\text{CaO}/\text{Fe} = 0.7$. The precise boundaries for regions B and C are yet to be fully delineated. However, current indications are that region C is bordered by the lines $\text{Fe}/\text{SiO}_2 = 1.14$ and $\text{Fe}/\text{SiO}_2 = 1.55$. Overall, the region C is illustrated by the compositions shown in Table 2.

Table 2 : Slag Compositions

<u>Examples</u>	<u>Fe/SiO₂</u>	<u>CaO/Fe</u>	<u>CaO/SiO₂</u>
1	1.55	0.17	0.27
2A	1.20	0.24	0.29
2B	1.14	0.24	0.27
3A	1.34	0.20	0.27
3B	1.47	0.15	0.22
4A	1.28	0.75	0.96
4B	1.21	0.92	1.11

Thus, considerable variability is possible with the iron based silicate slags able to be used in the present invention. This can enable a specific converting operation to be based on a slag composition best suited for use with locally available fluxes, or in accordance with the level of impurities reporting in the matte to be fed to the converting process conducted in that installation.

As indicated, the move to calcium ferrite slags, such as in the Mitsubishi process and followed in the proposal of Edwards et al, was in part to avoid the risk of slag foaming due to precipitation of magnetite. The calcium ferrite slags have a relatively high solubility limit for magnetite, thereby enabling them to reduce the tendency for foaming to occur. However, while iron based silicate slags have a lower solubility for magnetite, they can be used in the process of the present invention with little risk of foaming. This is believed to be due, in large part, to the requirements of the present invention for top-submerged injection. That is, that injection results in a more uniform or homogeneous slag phase in terms of agitation and of the dispersion therein of matte. Also, by not injecting gas into the blister copper phase, the present invention reduces the risk of producing a third phase comprising a slag/metal emulsion, with the risk of this triggering slag foaming.

It is found that the risk of foaming is able to be further reduced in the process of the present invention by the addition of a suitable reductant operable to reduce or prevent the formation of magnetite. Lump coal is a suitable reductant, in view of its tendency to float on the slag surface, such that slag is able to circulate to the coal under the agitation generated by submerged injection. The addition of lump coal is proposed in Edwards et al. However, this is to reduce the copper content of the slag for a given sulphur content in the blister copper. It is not to reduce the risk of foaming by preventing the formation of magnetite and that risk is obviated in Edwards et al by the choice of slag.

A flowsheet, illustrating the present invention in a form enabling continuous converting, is shown in Figure 4. The flowsheet shows a smelting/settling furnace, as well as a converting furnace operable in accordance with the present invention. The smelting/settling furnace can be of any type suitable for smelting

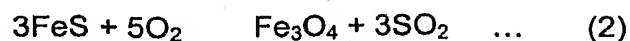
copper feed, comprising a copper sulphide concentrate, to produce a copper matte product and a slag. The slag may be discardable as shown, or suitable for further processing. After smelting, the matte and slag are allowed to settle to enable the slag to be discharged and the matte to be passed to the top-submerged lancing reactor furnace to be used in the converting stage.

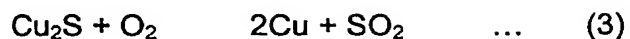
The matte may be of any grade suitable for converting to produce blister copper. It typically will range from 30% to 70% copper with various levels of Fe and S. The feed for the converting stage preferably is produced from an earlier smelting/settling operation in which a sufficient quantity of matte is produced to enable continuous converting over a sufficient interval of time. Thus, the matte may be stockpiled until such quantity is achieved.

The matte feed material for converting may be fed via a charging port in the roof of the top-submerged furnace, or via either a dedicated or specialised lance. The feed material need only be of a suitable size to allow it to be conveyed by the chosen feeding means, while it does not need to be dried. It is preferred that the matte feed material is granulated, for example as a product from smelting/settling furnace following the smelting of concentrate. However, at least part of the matte feed material may be supplied from the smelting/settling furnace in the hot, molten state.

In addition, other copper containing materials, such as reverts or scrap may be charged to allow efficient recovery of the contained copper. This may also be used to optimise control of process temperature.

In the process of converting, the Fe and S present in the matte are removed by reaction with oxygen by:





Thus, iron reports as iron oxide in the slag, while S reports as SO₂ in the converting furnace off-gas stream.

5 Two important factors during the converting operations are:

- (i) slag chemistry and copper losses to the slag, and
- (ii) the final quality of the blister copper.

On the issue of slag chemistry, typical converting operations in Pierce-Smith converters make use of the addition of silica to promote the formation of a
 10 molten iron silicate (fayalite) slag. Iron oxidised from the matte is taken up in that slag, reducing the formation of a solid magnetite phase. In large quantity, solid magnetite phase would make the slag unworkable, and lead to high copper losses due both to physical copper entrainment in the slag and to copper solubility.

As indicated herein, the present invention utilises a mode of top-
 15 submerged injection during converting, which obviates or overcomes perceived problems with iron silicate slags which, at least in part, contributed to the move away from those slags. Thus, the present invention preferably uses an iron based silicate slag, such as of fayalite or olivine composition. As detailed above, these slags provide significant benefits.

20 Our testwork has shown that a well controlled iron based silicate slag, such as of the fayalite type, enable acceptable levels of copper in slag. This is particularly so for slag to be recycled. Irrespective of the actual level of copper in recycled slag, that contained copper may be readily recovered by further processing as described earlier. Our testwork also has shown that, as detailed
 25 earlier herein, slag foaming is able to be prevented, or at least controlled.

As indicated above, blister copper product quality is of importance. The level of sulphur remaining in blister following processing is important, as too high a level requires additional processing downstream in order to remove it. An important relationship exists between the level of S in the blister copper and the level of copper reporting to slag. These levels are related to the oxygen potential needed to remove sulphur to a desired level and the effect of over-oxidising a portion of the copper to slag as Cu_2O , by reaction (4) detailed above. Results obtained in a pilot plant operation in accordance with the present invention showed that a low level of Cu in slag can be achieved together with a good level of S in blister copper, as indicated in Table 3.

Table 3 : Blister Quality v. Cu to Slag

<u>Example</u>	<u>Blister % S</u>	<u>Slag % Cu</u>
1	0.3	11.8
2B	0.02	35.8
3A	0.03	23.0
3B	0.4	14.3
4B	0.2	9.5

The process of Edwards et al is characterised by the level of sulphur in the blister copper being affected by the lance tip position. This necessitates the lance tip being as close as possible to the interface between the slag and blister copper phases. With the present invention, the position of the lance tip is important, as detailed earlier herein, but is not a significant factor in achieving good quality blister product.

Finally, it is to be understood that various alterations, modifications and/or additions may be introduced into the constructions and arrangements of parts previously described without departing from the spirit or ambit of the invention.

5 DATED: 6 April 2004

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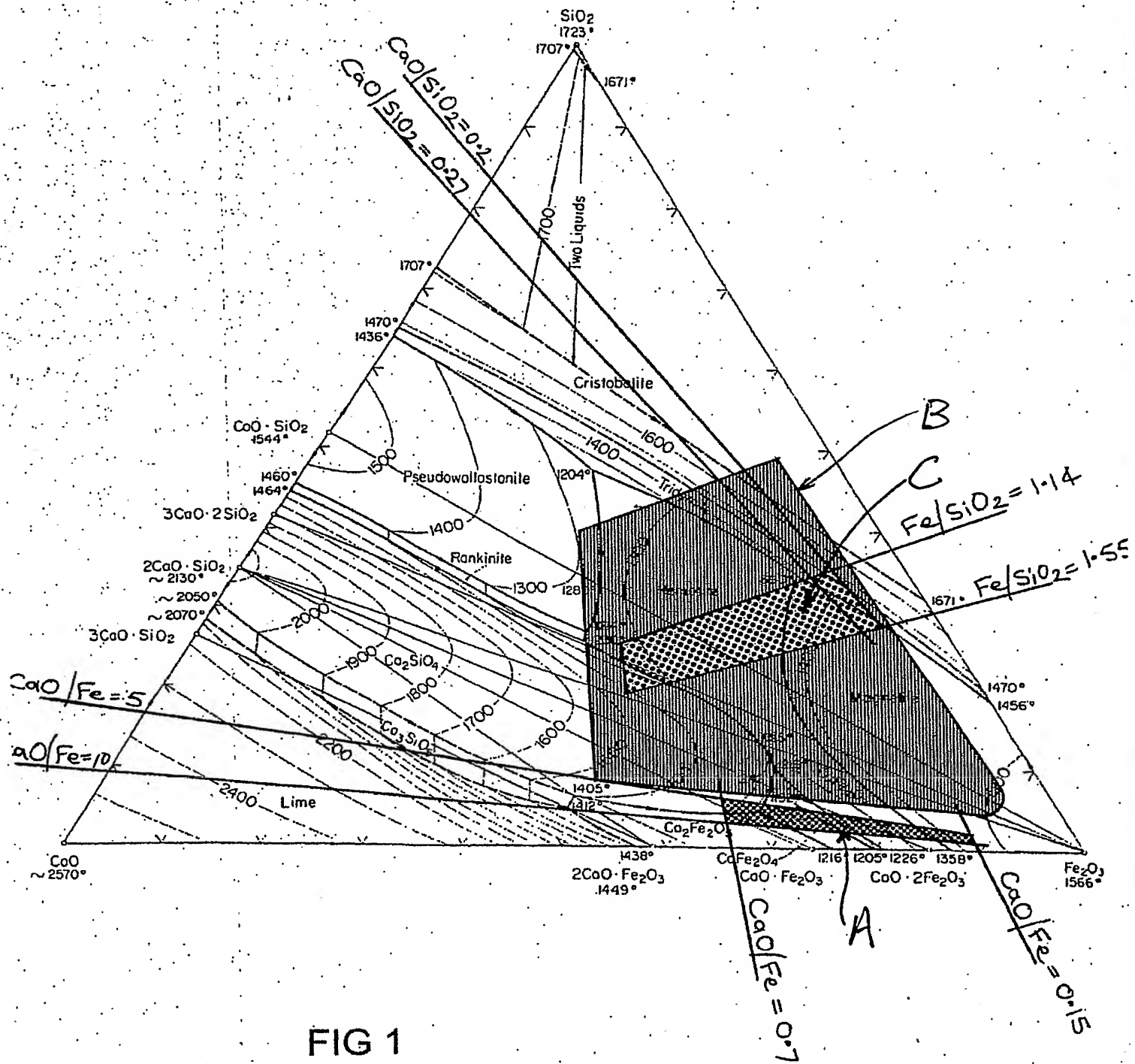


FIG 1

FIG 2

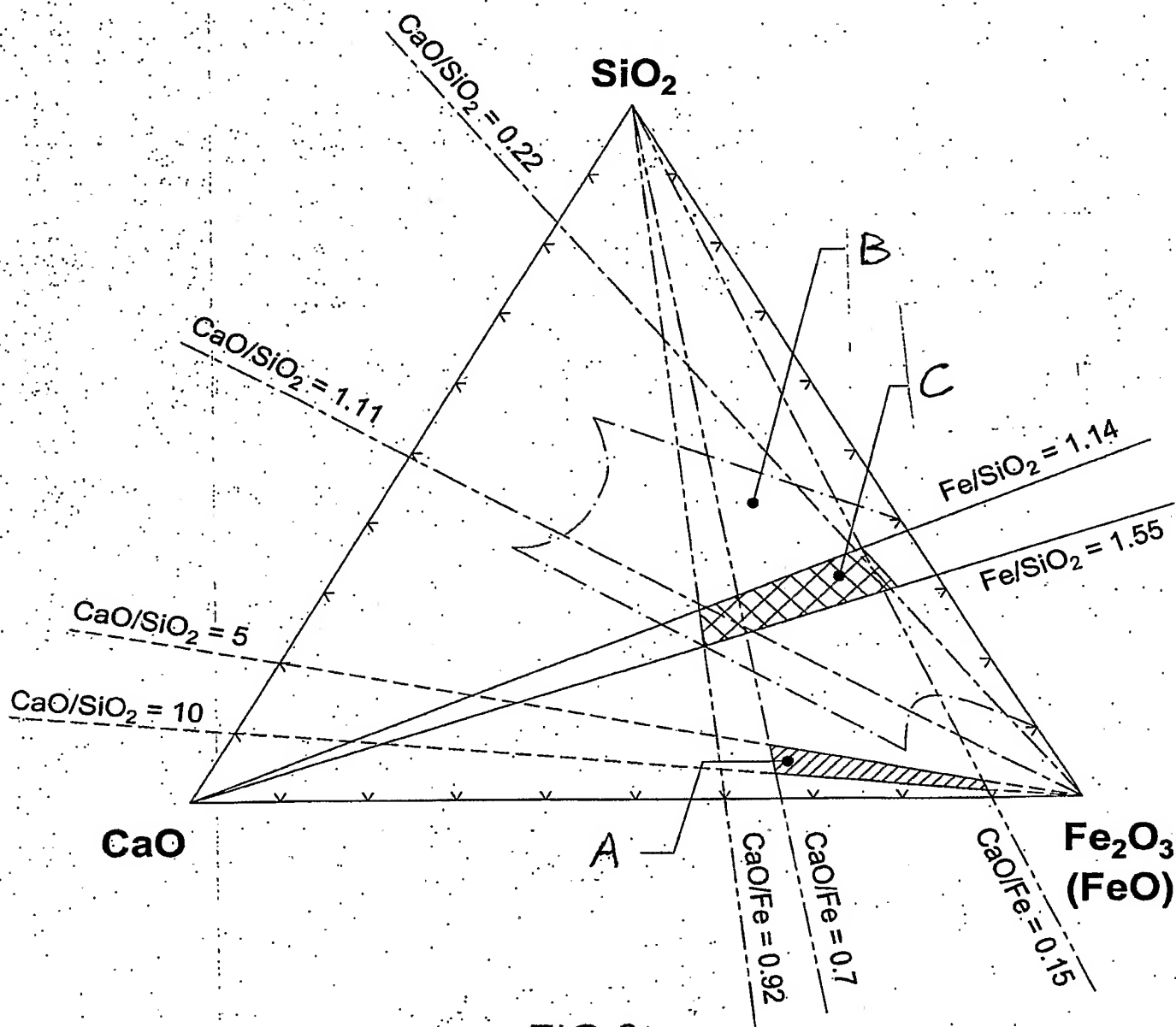


FIG 3

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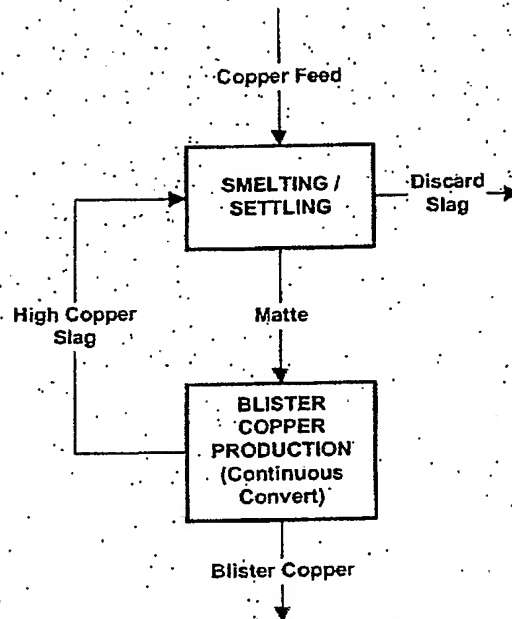


FIG 4